INVESTIGATION ON THE MECHANISMS OF BIO-PROCESSING VANADIUM SLAGS

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1 Introduction

The Highveld process (South Africa), the New Zealand steel vanadium recovery process (New Zealand), the Pan-steel process (China) and the NTMK duplex process (Russia) are the most common methods used for the recovery of vanadium from V-containing hot metal. Despite the difference of the vanadium containing hot metals and type of reactors, vanadium is oxidised into a vanadium slag by oxygen in all the four process. The Linz-Donawits decarburisation process followed by the pre-oxidation of the hot metal from iron making is the most practised technique[1].

Extensive research works have been devoted to the recovery of vanadium from vanadium-bearing slags. Oxidation of molten slag with pure oxygen in the presence of CaO and leaching with sulfuric acid to extract vanadium was investigated[2]. CaV_2O_5 and $Ca_2V_2O_7$ were formed and about 90% of vanadium was recovered. The recovery of vanadium by means of high pressure oxidative leaching from vanadium slag was also investigated[3]. During the leaching process, degradation of fayalite and spinel phases by sulfuric acid was noticed. Vanadium and iron were extracted into the solution whilst silicon and titanium remained in the residue. The recovery of vanadium from V-slag is also processed by the well-known roasting-leaching process[4]. The slag is first of all roasted under alkaline conditions in presence of one or a combination of sodium salts such as NaCl, Na_2CO_3 and Na_2SO_4 under oxidizing atmosphere for the conversion of the vanadium into water-soluble sodium vanadate. Lime can also be used as well in the roasting process to form calcium vanadate phases to be leached with acid or alkali[5]. However, high production costs, complicated processes and the emissions of polluting gases limit further applications of these technologies.

New environmentally friendly process for treatment of low grade ores are compulsory due to the diminution of high grade metal reserves and new strict environmental regulations[6]. Lately, bioleaching has come forth as an efficient technology for the leaching of vanadium either from its slags or ores. The leaching process is carried out by microorganisms such as bacteria and fungi. Extraction of 83% vanadium by bioleaching of exhaust catalysts in the presence of iron was achieved[7]. Three different species of microbial systems: Acidithiobacillus thiooxidans (autotrophic bacteria), Pseudomonas putida (heterotrophic bacteria) and

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Aspergillus niger (fungi) have also been used for the recovery of vanadium from vanadium Linz-Donawits (LD) converter slag[8].

Based on previous work done using bacteria, it was demonstrated that during the leaching process, gluconic (Gl), citric (Cit) and oxalic (Ox) acids are generated. The present work is an investigation on a simulation of bioleaching using similar commercial acids on the raw and roasted vanadium bearing slag in order to understand their mutual contribution during the vanadium dissolution.

2 Materials and methods

2.1 Materials

The vanadium slag used in the present study was obtained from Rhovan Glencore Mine based in South Africa and was generated from a steelmaking plant. The chemical composition of the raw and roasted slag was determined using X-ray Fluorescence spectrometer (XRF) Rigaku ZSX Primus II. Identification of mineral phases present in the raw and roasted slag was done using X-ray Diffraction (XRD) Rigaku Ultima IV. The dissolved vanadium from the sample was analysed using atomic absorption spectroscopy (AAS). Reagents used in this experiment were analytical high grade and provided by MERCK.

2.2 Methods

2.2.1 Roasting process

The sample was crushed and then pulverised up to 100 % passing 75µm. The pulverised sample was mixed with 10 wt% sodium carbonate. The mixture was pelletized and heated at 800^{o}C for 2 hours in a muffle furnace. The roasted slag was left to cool down inside the furnace for 12 hours. It was then analysed on the XRD to assess the formation of new phases.

2.2.2 Leaching process

The raw and roasted slags were leached separately using gluconic, citric, and oxalic acids at 50, 100, 150 mM concentration. The leaching experiments were carried out at room temperature, 150 rpm of agitation and 2% of solid- liquid ratio. The leached solution was collected for analysis after 20, 100, and 180 minutes. A 250ml beaker in a shaking water bath was used in the leaching process.

3 Results and discussion

3.2 Characterisation of the raw slag

The chemical composition of the as received sample is shown in Table 1. It can be seen

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that the slag contains a considerable amount of vanadium (2.57%). Major elements present are aluminium (32.54%) and calcium (13.54%).

Table 1: Chemical composition of the slag

Component	Na_2O	MgO	Al_2O_3	SiO_2	CaO	V_2O_5	Fe_2O_3
% Oxide	3.25	7.03	61.49	1.54	18.94	4.58	0.84

The sample was analysed with XRD and the results presented in Figure 1. Figure 1 shows the mineralogical phases present in the slag and it can be noticed that vanadium is present in the slag in the form of calcium vanadium oxide ($Ca_2V_2O_7$) and vanadium oxide (V_2O_5). It is also associated with other components such as Fe, Al and Mg in the form of a spinel. Presence of grossite phase ($Ca\ Al_4O_7$) in the sample was also noticed.

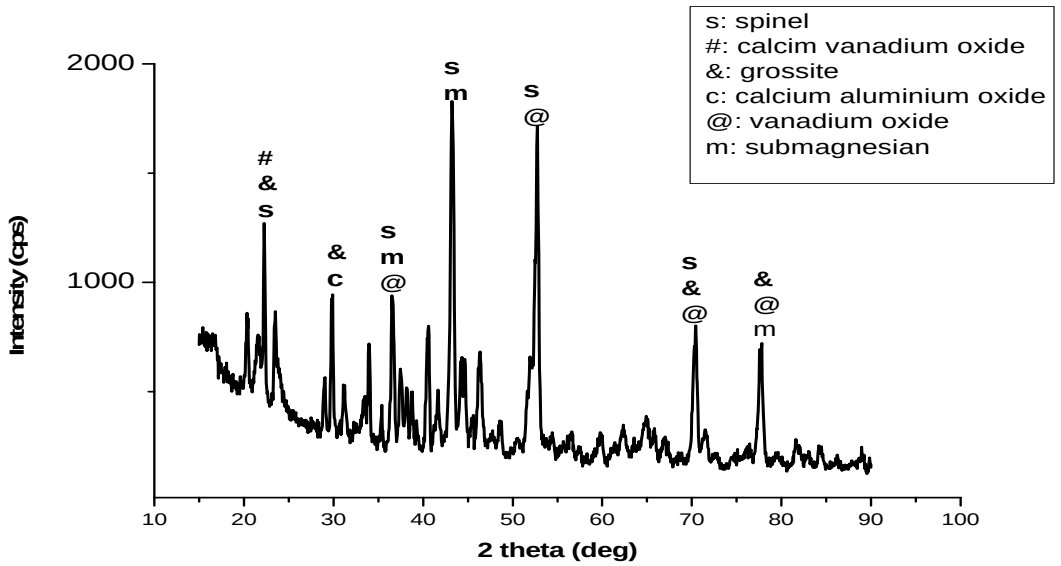

Figure 1: XRD pattern of the V-slag sample

3.3 Leaching experiments

3.3.1 The effect of acid concentration on the leaching of vanadium from raw and roasted slag

The dissolution of vanadium from the raw and roasted slag while varying the concentration of different acids is given in Figure 2. It can be seen that the average dissolution of vanadium from the raw sample in the three organic acids is very low. This can be explained by the fact that vanadium does not dissolve easily in aqua medium due to its refractoriness character. Vanadium present in the slag may be found in its stable oxidation state V or in the form of oxide compounds which are generally difficult to pass into the solution. Results

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presented in Figure 2 shows that a maximum of 46,2ppm (2.5%), 61,2ppm (3.4%) and 110,73ppm (6.1%) of vanadium was dissolved while leaching with 150mM of gluconic, citric and oxalic acids respectively. The dissolution of vanadium is very high on the roasted slag compared to the raw and about 1531.23ppm, 1121.73ppm and 1004ppm were dissolved using Gl, Ci and Ox acid respectively at a concentration of 150mM. Vanadium has a higher dissolution at a very low Gl acid concentration (50mM).

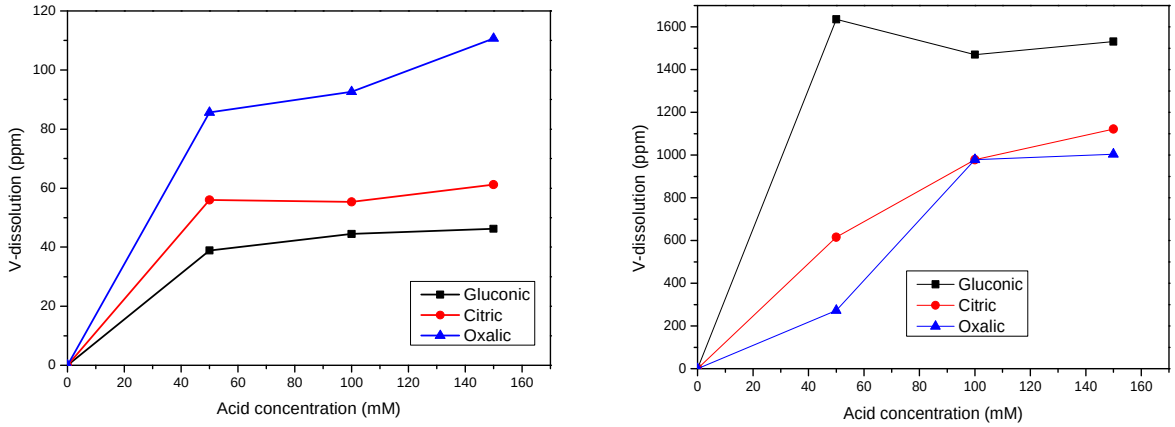

Figure 2 : Effect of organic acids concentration on the recovery of vanadium from the raw (left) and roasted slag (right)

3.2.2 The effect of leaching time on the dissolution of vanadium from roasted slag sample.

The effect of the leaching time on dissolution of vanadium was investigated and the results presented in Figure 3. It was observed that the rate of dissolution in Gl and Ox acids increases with increase in time up to 60mins. Further increase in time has no much effect on dissolution in Gl acid but decreases in Ox acid. Leaching time has insignificant effect on dissolution of vanadium in Ci acid.

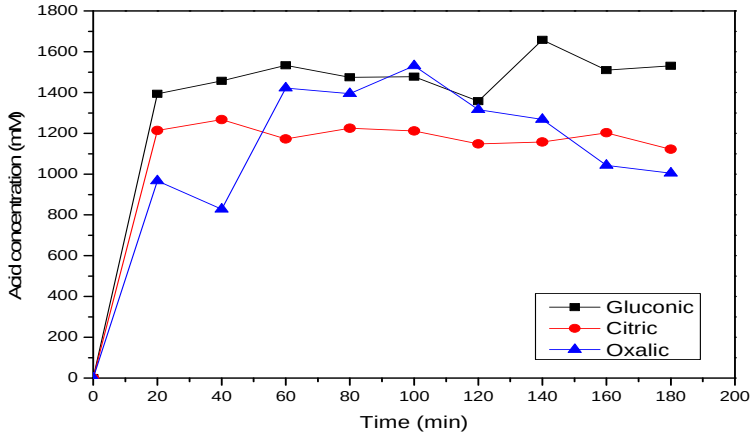

Figure 3: Effect of leaching time on the dissolution of vanadium from the roasted slag

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Conclusion

The leaching experiments indicated that vanadium can be leached from roasted V-bearing slag using very low concentrations of gluconic, oxalic and citric acid. The results suggest that gluconic acid is the best leachate followed by citric acid and then oxalic acid. Optimum leaching time using all acids is 60mins. Further studies needs to target bacteria that produces more of gluconic acid as compared to the other two.

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